



readily achieved, however, very fine ore particles can be difficult to separate because they can be held in suspension in the liquid. Solid/liquid separation procedures, such as those described earlier in Chapter 4.4, must be employed to obtain a clear liquor, free from suspended matter.

The intention of the leaching reaction is to dissolve the mineral containing the desired metal so that metal ions are obtained in solution. In doing so, however, it is inevitable that elements will be brought into solution which

- are not wanted in the process and which may interfere with subsequent processing, or
- will result in unacceptable impurity levels in the final product.

Having obtained the raw leach liquor, further separation treatment must usually be carried out

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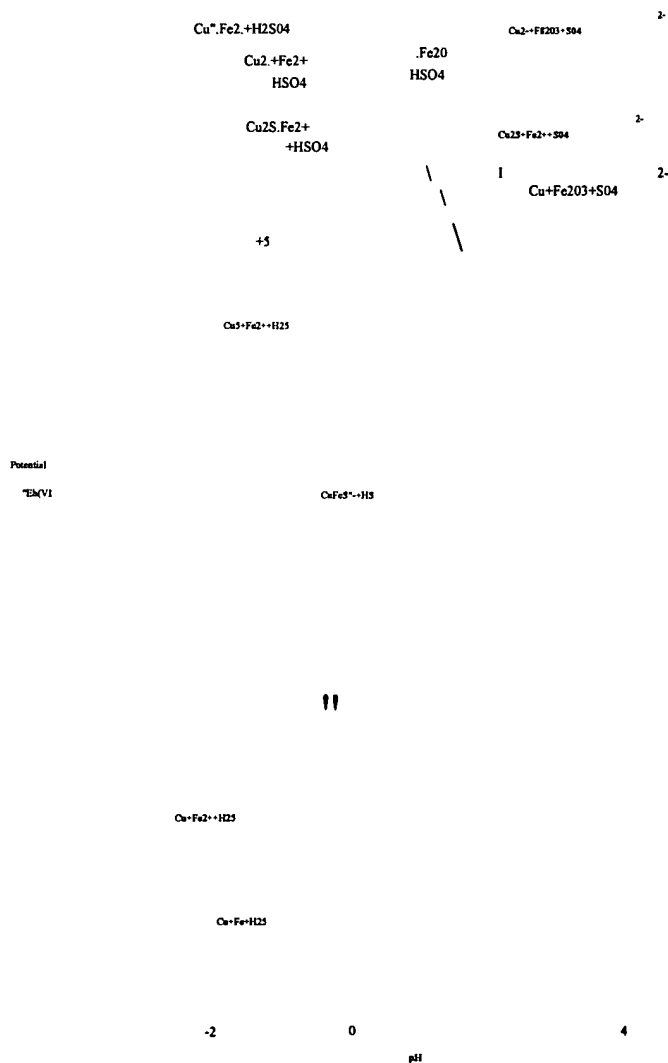


FIG.6.2.17 **F<sub>2</sub>-pH** diagram for the Cu-Fe-S-H<sub>2</sub>O system in absence of pyrite at 25°C (1st Tutorial) {Copyright Met. Soc. AIME)

to lower the concentration of unwanted elements in the solutions. Alternatively, the desired metal may be selectively removed from the solution leaving behind the impurities.

### 6.2.2.1. Selective **Precipitation**

The selective **precipitation** of metal ions from leach solutions is used extensively for the **purification** leach liquors.

Control of potential and **pH**. Perhaps the most widely used method of removing impurities is controlled changes in **pH**. Figure 6.2.19 summarises the thermodynamic data for the **precipitation** metal hydroxides from solutions at 25°C. (Monhemius, b). In solutions whose compositions lie to right of the lines on this diagram **precipitation** of the hydroxide will occur. The diagrams may also be used to estimate the theoretical solubilities of the ions in equilibrium with the metal hydroxide at any given **pH**. In the case

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FIG. 6.2.18

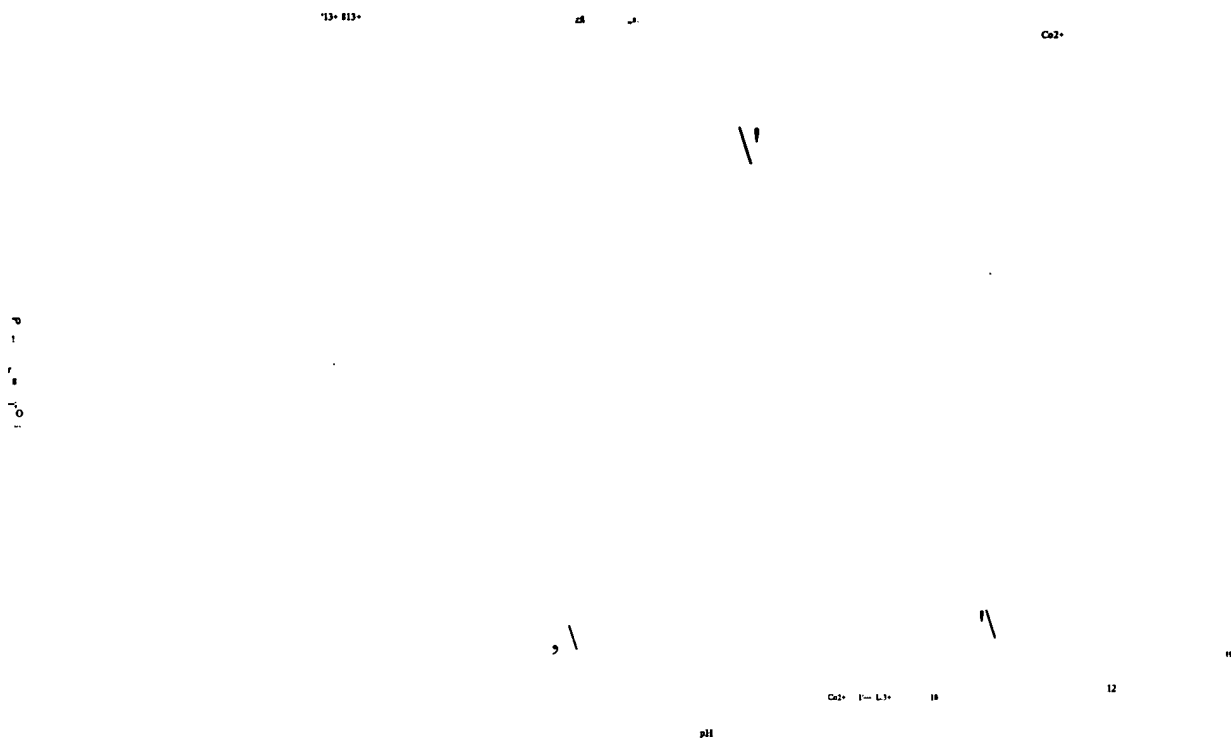


FIG. 6.1.19 The hydroxide **precipitation** diagram at 25°C (Monhemius, b» (Copyright IMM) of manganese, for example, at pH 8 the solubility of  $Mn^{2+}$  in the solution is 1 mol; **changing the pH** to

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a value of 10 results in the **precipitation** of manganese hydroxide with only  $10^{-5}$  mol of  $Mn^{2+}$  ions remaining in solution.

The **precipitation** of metal sulphides may also occur in the presence of S gas, (Figure 6.2.20). This reaction may be utilised in **purification** reactions but the information is also useful in analysing leaching conditions. For example, in the leaching of sulphide ores in acidic non-oxidising conditions, S may produced during the reaction. The presence of S in the leach liquor can cause the **precipitation** of secondary metal sulphides which it is intended to coextract from the ores. These precipitated sulphides would then be lost in the discarded leach residues.

#### EXAMPLE **Precipitation** of nickel and cobalt sulphide.

The separation of nickel and cobalt from solutions containing ferrous sulphate can be carried out using S. The equilibrium Fe, Ni and Co concentrations in equilibrium with S 1 atm. at pH 1 at 25°C are 1, 0.01, 0.0001 M respectively. Thus close control of pH allows separation of the base metals from the solution, provide the kinetics of the reaction are favourable. (See Example in Chapter 6.4.2).

**Thermal precipitation.** The **precipitation** of solids from aqueous solutions may also be carried out by simply altering the temperature of the solutions - a process referred to as **thermal precipitation**. Sufficient

thermodynamic data are available to allow the calculation of the conditions necessary for thermal precipitation in the  $\text{CuSO}_4$  -  $\text{H}_2\text{SO}_4$  -  $\text{H}_2\text{O}$  system, (Kwok and Robbins). Figures 6.2.21 a-c show the phases present in this system as a function of metal, sulphate and hydrogen ion activity at 25, 100 and 200°C. It is apparent that the regions of stability of the various phases vary significantly with temperature. It should be noted, however, that the pH quoted in these diagrams is the pH at the reaction temperature, this is not necessarily the pH of the solution before it was heated to temperature. To determine how the pH of the solution varies with temperature it is necessary to consider the interactions of the various ions in the solution with hydrogen ions. In the present example the effects of the following equilibria must be taken into account at each reaction temperature.



Figure 6.2.22 shows how the equilibrium constants for these reactions vary with reaction temperature. Given the equilibrium constants for the reactions and the activity coefficients of the various species in solution these equations can be solved simultaneously for any given concentration of  $\text{CuSO}_4$ . The results of such calculations are shown in Figure 6.2.23 for a solution of 0.1 M  $\text{CuSO}_4$  0.01 M  $\text{H}_2\text{SO}_4$  initially at 25°C. Line B shows how the pH of the solution varies with reaction temperature. Line A represents the solubility limit of  $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$  as a function of temperature for the same copper and acid concentrations as quoted above. Thus it can be seen that to obtain precipitation of  $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$

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a)  $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  system at  $25^\circ\text{C}$

FIG. 6.2.22 Variation of equilibrium constants for various reactions in  $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  system with temperature (Kwok and Robbins) (Copyright AIIME)

#### EXAMPLE The removal of iron ions from solution

Phase diagrams have the same limitations as other equilibrium representations in that they are restricted to the compounds considered and they give no information on the kinetics of the reactions. These limitations are clearly illustrated in the case of iron **precipitation**. Iron is probably the most common impurity which is removed from leach solutions.

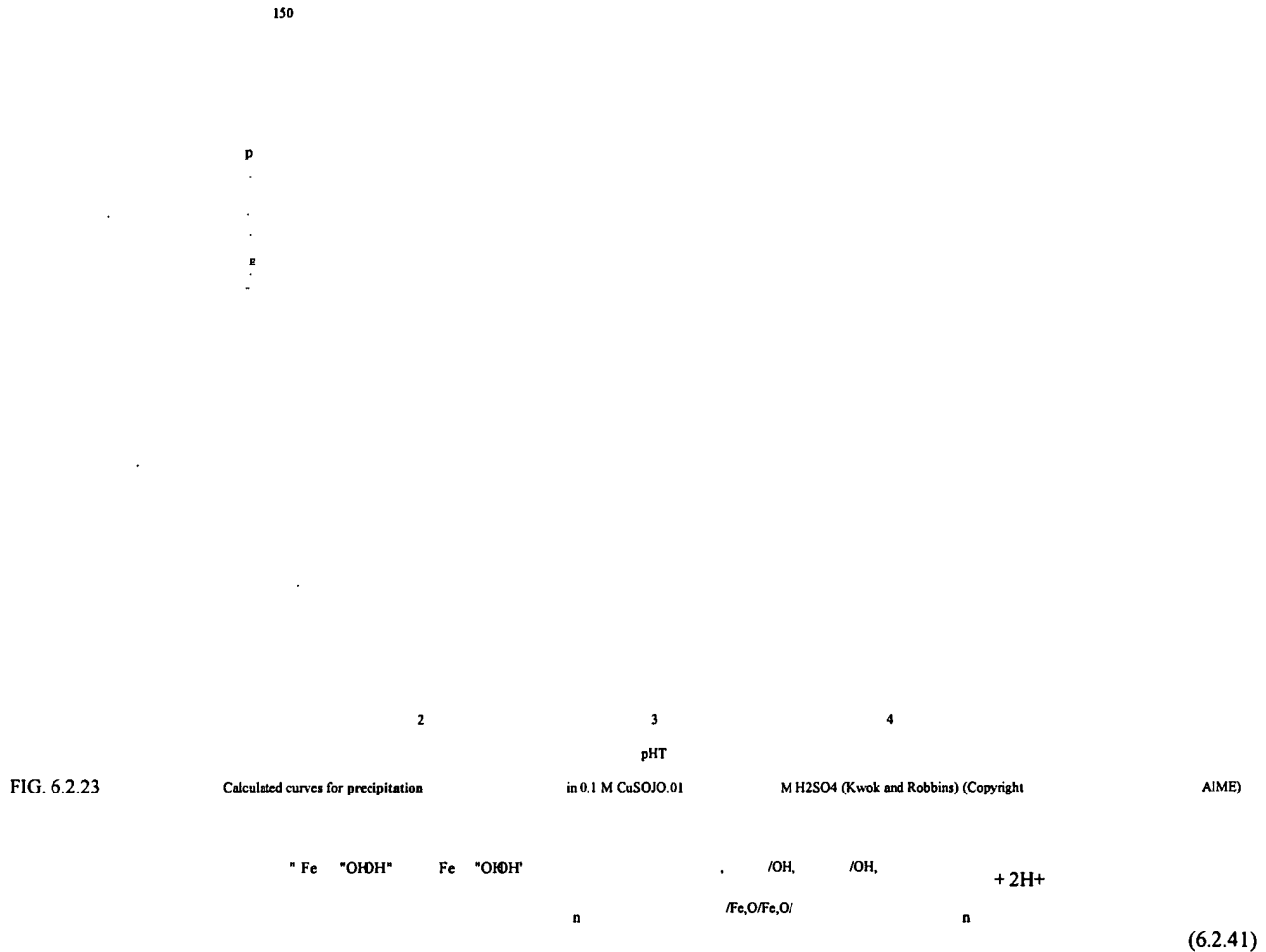
In the presence of ferric ions in the solution,  $\text{Fe}^{3+}$ -hydroxyl complexes are formed. These iron complexes attain a true equilibrium in the solution in the absence of gaseous oxygen. When the solution conditions are changed to obtain the **precipitation** of  $\text{Fe}(\text{OH})_3$  it appears that these complexes form polymers, which only eventually lead to the formation of a precipitate, i.e.



(6.2.4)

If the **pH** is raised rapidly these lengthy polymers become cross-linked via hydroxyl bridges and iron hydroxide gel colloids are formed. This is clearly an undesirable structure since the poor settling properties of the iron gel make solid/liquid separation difficult.

If insufficient base is added to cause immediate gel formation, but there is still sufficient to favour **precipitation**, O-bridges are formed in the structure



This structure is a precursor to goethite (FeOOH) or hematite (Fe<sub>2</sub>O<sub>3</sub>) **precipitation**. In summary, the rapid addition of excess base, poor agitation and low temperatures promote gel formation; high temperatures, controlled additions and good agitation can result in the formation of discrete goethite, magnetite or hematite crystals.

The presence of other anions in the system can considerably increase the number of different compounds which may be precipitated from solution. This is illustrated in Figures 6.2.24 a) and b) for the Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-O<sub>2</sub> system. (Posnjak and Merwin). **Precipitation** will occur when the composition of the solution exceeds the values indicated by the three dimensional surface in these figures.

Considerable improvements in zinc recovery have been possible through the development of efficient **precipitation** techniques. (Dutrizac) Iron is commonly associated with zinc sulphide concentrates both as a replacement for zinc in sphalerite and as separate minerals such as pyrite or chalcocopyrite. Before hydrometallurgical treatment these concentrates are converted to oxides. Roasting above 900°C results in some of the iron forming hematite, Fe<sub>2</sub>O<sub>3</sub> but most combines with the zinc oxide to form zinc ferrite, ZnO·Fe<sub>2</sub>O<sub>3</sub>. During a conventional sulphuric acid leach free zinc oxide is dissolved while zinc ferrite is not. This results in considerable zinc losses in the process. It has long been known that with excess sulphuric acid at 100°C the zinc ferrite can be dissolved but this also results in



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FIG. 6.2.24 System  $\text{Fe}_2(\text{SO}_4)_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ , a) Polytheneffl 50°C to 200°C, 0 to 40%  $\text{SO}_4$ .

unacceptably high iron concentrations in the leach liquor. The simple neutralisation

of the solution results, as stated

above in the precipitation

of a gel, making solid/liquid

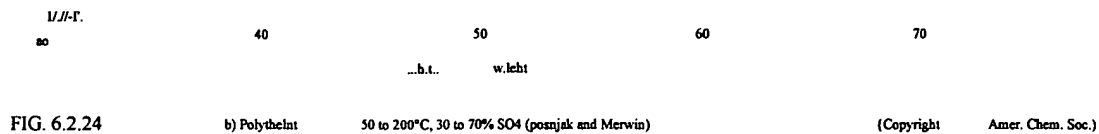
separation difficult.

It was found, however, that precipitation

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$\text{Fe}(\text{OH})(\text{SO}_4)$



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could be carried out without undue difficulty by adding NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup> or K<sup>+</sup> ions to the solution and adjusting the pH of the solution to 1.1 -1.5 by calcine addition. Under these conditions a crystalline phase known as "jarosite" is readily precipitated, leaving a zinc-rich solution containing only 1-3 g l-Fe. The jarosite is readily separated from the solution and contains only small amounts of zinc substituted in the jarosite lattice. The jarosites can be formed with a wide range of cations and have a general formula M Fe<sub>3</sub> (SO<sub>4</sub>)<sub>2</sub> (OH)<sub>6</sub> where M is NH<sub>4</sub><sup>+</sup>, H<sub>3</sub>O<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> etc. The planes of solubility of ammonium jarosites are shown in Figure 6.2.25. Although the jarosite process has its limitations, in that the iron content of the precipitate is low and difficulties can occur with the long term stability of the compounds in residue dumps, it has resulted in significant overall improvements in zinc recover

FIG. 6.2.25 System Fe<sub>2</sub>(SO<sub>4</sub>)-H<sub>2</sub>SO<sub>4</sub>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O at 100°C. Planes of solubility of (NH<sub>4</sub>,H<sub>3</sub>O)Fe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH), and (NH<sub>4</sub>,H<sub>3</sub>O)Fe(SO<sub>4</sub>)<sub>2</sub> (Kershaw and Pickering) (Copyright Met. Soc. AIME)

### 6.2.2.2 Ion Exchange

The separation of ions from solution is, with increasing frequency, being carried out using ion exchange processes. Metal ions in solution can exchange with specific ions contained in a solid or second liquid phase.

These reactions are reversible and stoichiometric and can provide convenient methods of,

- „ removing unwanted ions from aqueous solutions, and
- „ increasing the concentrations of selected metal ions in the solution.